

0/500283

DT04 Rec'd PCT/PTO 29 JUN 2004

Substitute Pages 4, 5, 5/1, 7, 8, 8/1, 16 & 17 for publication

becomes difficult to introduce sufficient nitrogen into material and the synthesis of the compound containing Ti(IV) which has nitride bond is impossible, and the responsibility to visible light of the material is too low to absorb the visible light of around 600nm. Accordingly, the method for synthesis of the compound containing Ti(IV) which has nitride bond is an epoch-making invention.

SUMMARY OF THE INVENTION

The first one of the present invention is a photo-catalyst containing titanium fluoride nitride comprising, $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ or a compound represented by $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$ prepared by doping at least one metal Me selected from the group consisting of alkalis or alkali metals on $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ (wherein, b is 0.1 to 1, c is 0.1 to 1 and a is a value to maintain Ti(IV) and is decided in relation to b and c). Desirably, the present invention is the photo-catalyst containing titanium fluoride nitride, wherein $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ possesses anatase structure and $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$ possesses perovskite to anatase structure. Further desirably the present invention is the photo-catalyst containing titanium fluoride nitride to which at least one promoter selected from the group consisting of Pt, Ni and Pd is loaded.

The second one of the present invention is a photo-catalyst for water splitting containing titanium fluoride nitride comprising $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ or a compound represented by $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$ prepared by doping at least one metal Me selected from the group consisting of alkalis or alkali metals on $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ (wherein, b is 0.1 to 1, c is 0.1 to 1 and a is a value to maintain Ti(IV) and is decided in relation with b and c). Desirably, the second one of the present invention is a photo-catalyst for water splitting containing titanium fluoride nitride wherein $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ possesses anatase structure and $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$ possesses perovskite to anatase structure. Further desirably the second one of the present invention is a photo-catalyst for water splitting containing titanium fluoride nitride to which at least one promoter selected from the group consisting of Pt, Ni and Pd is loaded.

The third one of the present invention is a method for preparation of a photo-catalyst represented by $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ by baking titanium diammonium fluoride halide containing at least F represented by $(\text{HH}_4)_2\text{TiF}_d\text{X}_{6-d}$ and ammonium halide by the ratio of equimolar or by the ratio of slightly excess of ammonium halide at the maximum temperature

from 200°C to 500°C, desirably from 300°C to 450°C so as to form a starting material, then said starting material is nitrogenated by thermal synthesis in ammonia atmosphere containing from 0.02% to 10.00% of oxygen, air or water to ammonia by reduced mass to oxygen atom at the maximum temperature from 350°C to 700°C, desirably from 400°C to 600°C over than 5 hours.

The fourth one of the present invention is a method for preparation of a photo-catalyst represented by $\text{SrTi(IV)O}_a\text{N}_b\text{F}_c$ by baking titanium di-ammonium fluoride halide containing at least F represented by $\text{TiF}_x\text{X}_{6-x}$ and/or $(\text{HH}_1)_2\text{TiF}_d\text{X}_{6-d}$ and at least one selected from the group consisting of SrO , SrOH and SrX so as to form a starting material or SrTiF_6 , then said starting material or SrTiF_6 is nitrogenated by thermal synthesis in ammonia atmosphere containing from 0.02% to 10.00% of oxygen, air or water to ammonia by reduced mass to oxygen atom at the maximum temperature from 350°C to 700°C over than 5 hours.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is the X ray diffraction spectrum of the compound of Example 1 containing titanium fluoride nitride after nitration.

Fig.2 is the UV·Visible ray absorption characteristic curve of the compound of Example 1 containing titanium fluoride nitride after nitration (obtained by diffuse reflectance spectrum. And so forth in followed Figures).

Fig.3 shows the change of H_2 generation by time lapse from 10vol% methanol aqueous solution by visible light longer than 420nm using photo-catalyst prepared by loading 3% of platinum on the compound of Example 1 containing titanium fluoride nitride after nitration.

Fig.4 shows the change of O_2 generation by time lapse from AgNO_3 aqueous solution by visible light longer than 420nm using the photo-catalyst of Fig.3.

Fig.5 is the X ray diffraction spectrum of the compound of Example 2 containing titanium fluoride nitride after nitration.

Fig.6 is the UV·Visible ray absorption characteristic curve of the compound of Example 2 containing titanium fluoride nitride after nitration

Fig.7 shows the change of H_2 generation by time lapse from 10vol% methanol aqueous solution by visible light longer than 420nm using photo-catalyst prepared by loading 3% of platinum on the compound of Example 2

dioxide P25 on the market after baked of Comparative Example 1.

Fig.21 shows the UV-Visible ray absorption characteristic curve of Fig.20.

Fig.22 is the X ray diffraction spectrum of the nitride compound prepared by baking titanium dioxide of Comparative Example 2 in the atmosphere of ammonia NH_3 at the maximum temperature 6000°C for 15 hours.

Fig.23 is the X ray diffraction spectrum of the nitride compound of Fig.22.

Fig.24 shows the X ray diffraction spectrum of strontium titanate SrTiO_3 on the market.

Fig.25 shows the UV-Visible ray absorption characteristic curve of Fig.24.

Fig.26 is the X ray diffraction spectrum of the compound prepared by temperature programmed strontium titanate SrTiO_3 on the market of Comparative Example 4 to 4000°C (673K) in the atmosphere of ammonia NH_3 by temperature-programming speed of 10K/minute then maintain this temperature for 5 hours.

Fig.27 shows the UV-Visible ray absorption characteristic curve of Fig.26.

DESCRIPTION OF THE PREFERRED EMBODYMENT

The present invention will be illustrated more in detail.

A. The photo-catalysts of the present invention can be obtained by satisfying the essential factors described in the claims.

As the compound having chemical composition of $(\text{HH}_4)_2\text{TiF}_d\text{X}_{6-d}$; $(\text{HH}_4)_2\text{TiF}_6$ and $(\text{HH}_4)_2\text{TiF}_2\text{XCl}_4$ can be mentioned as the desirable one.

As the material to obtain a starting material to prepare the compound having chemical composition of $\text{SrTi(IV)O}_a\text{N}_b\text{F}_c$, the mixture of TiF_4 and SrF_2 can be mentioned as the desirable one.

EXAMPLE

The present invention will be illustrated more specifically according to the Examples, however, not intending to limit the scope of the present invention.

Example 1

As the first step, diammonium hexafluorotitanate $((\text{NH}_4)_2\text{TiF}_6)$ and ammonium chloride (NH_4Cl) were mixed by 1:1 molar ratio. Then the mixture was contained into a golden tube and the opening was sealed by welding. This golden tube was baked at 400°C (673K) in an electric furnace for 12 hours. After baking, synthesis by nitration was carried out under ammonium stream containing oxygen (ammonia flow rate: $0.2\text{dm}^3\cdot\text{min}^{-1}$, oxygen flow rate: $1\text{cm}^3\cdot\text{min}^{-1}$) at the temperature of 600°C (873K) for 12 hours.

Loading of platinum on said material was carried out as follows. Namely, 0.00357dm^3 of $0.1\text{mol}\cdot 0.1\text{mol}\text{dm}^{-3}$ tetraamminedichloro platinum $\text{Pt}(\text{NH}_4)_4\text{Cl}_2$ solution (Pt 3wt%) was impregnated to 0.3g of said material on a water bath and water was evaporated, then reduced by hydrogen at 300°C (573K) for 2 hours.

The X ray diffraction spectrum of the material after baking are shown in Fig.1. All diffraction peaks in Fig.1 are belonging to TiNF (refer to Paper: Angew. Chem. Int. Ed. Engle.27 (1988) No.7) and the generation of TiNF is confirmed. UV-Visible ray absorption characteristic curve of said material (obtained by diffuse reflectance spectrum) is shown in Fig.2. From Fig.2, it become clear that said material absorbs visible light shorter than 600nm . From the result of elemental analysis, the ratio of Ti:O:N:F is 1:1.76:0.13:0.10 ($\text{TiO}_{1.76}\text{N}_{0.13}\text{F}_{0.10}$).

In Fig.3 the change of H_2 generation amount by time lapse when 0.2g of material to which 3% of platinum is loaded is dispersed in 0.310dm^3 of 10vol.% methanol aqueous solution and visible light longer than 420nm is irradiated. 300w xenon lamp is used as the light source and the visible light shorter than 420nm is cut off by a cut off filter. As shown in Fig.3, it is understood that said material can generate hydrogen constantly from methanol aqueous solution by the irradiation of visible light longer than 420nm . Further, in Fig.4 the change of oxygen generation amount by time lapse, when 0.2g of above material is suspended into 0.310dm^3 of $0.01\text{mol}\text{dm}^{-3}$ AgNO_3 aqueous solution and visible ray longer than 420nm is irradiated. The reaction is carried out by same condition mentioned above. From Fig.4, it become clear that above mentioned material can generate oxygen from silver nitrate aqueous solution under irradiation of visible light longer than 420nm .

As mentioned above, it is confirmed that TiNF has an ability to reduce

CLAIMS

1. A photo-catalyst containing titanium fluoride nitride comprising, $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ or a compound represented by $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$ prepared by doping at least one metal Me selected from the group consisting of alkalis or alkali metals on $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$, wherein, b is 0.1 to 1, c is 0.1 to 1 and a is a value to maintain Ti(IV) and is decided in relation to b and c .

2. The photo-catalyst containing titanium fluoride nitride of claim 1 to which at least one promoter selected from the group consisting of Pt, Ni and Pd is loaded.

3. The photo-catalyst containing titanium fluoride nitride of claim 1, wherein $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ possesses anatase structure and $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$ possesses perovskite to anatase structure.

4. The photo-catalyst containing titanium fluoride nitride of claim 3 to which at least one promoter selected from the group consisting of Pt, Ni and Pd is loaded.

5. A photo-catalyst for water splitting containing titanium fluoride nitride comprising, $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ or a compound represented by $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$ prepared by doping at least one metal Me selected from the group consisting of alkali or alkali metals on $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$, wherein, b is 0.1 to 1, c is 0.1 to 1 and a is a value to maintain Ti(IV) and is decided in relation with b and c .

6. The photo-catalyst for water splitting containing titanium fluoride nitride of claim 5 to which at least one promoter selected from the group consisting of Pt, Ni, Ru and Pd is loaded.

7. The photo-catalyst for water splitting containing titanium fluoride nitride of claim 5, wherein $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ possesses anatase structure and $\text{MeTi(IV)O}_a\text{N}_b\text{F}_c$ possesses perovskite to anatase structure.

8. The photo-catalyst for water splitting containing titanium fluoride nitride of claim 7 to which at least one promoter selected from the group consisting of Pt, Ni and Pd is loaded.

9. A method for preparation of a photo-catalyst represented by $\text{Ti(IV)O}_a\text{N}_b\text{F}_c$ by baking titanium di-ammonium fluoride halide represented by $(\text{HH}_4)_2\text{TiF}_d\text{X}_{6-d}$ which contains at least F and ammonium halide by the ratio of equimolar or by the ratio of slightly excess of ammonium halide at the maximum temperature from 200°C to 500°C so as to form a starting material, then said starting material is nitrogenated by thermal synthesis in ammonia atmosphere containing from 0.02% to 10.00% of oxygen, air or water to ammonia by reduced mass to oxygen atom at the maximum temperature from 350°C to 700°C for over than 5 hours.

10. A method for preparation of a photo-catalyst represented by $\text{SrTi(IV)O}_a\text{N}_b\text{F}_c$ by baking titanium di-ammonium fluoride halide represented by $\text{TiF}_x\text{X}_{6-x}$ and/or $(\text{HH}_4)_2\text{TiF}_d\text{X}_{6-d}$ which contains at least F and at least one compound selected from the group consisting of SrO, SrOH and SrX so as to form a starting material or SrTiF_6 , then said starting material or SrTiF_6 is nitrogenated by thermal synthesis in ammonia atmosphere containing from 0.02% to 10.00% of oxygen, air or water to ammonia by reduced mass to oxygen atom at the maximum temperature from 350°C to 700°C for over than 5 hours.